36

ON THE RAMAN SPECTRA OF ETHYLENE CHLORHYDRIN AND *n*-PROPYL CHLORIDE IN THE VAPOUR STATE*

By MONOMOHAN MAZUMDER

Optics Department, Indian Association for the Cultivation of Science, Calcutta-32.

(*Received for publication, June* 28, 1955)

Plate VIII

ABSTRACT. The Raman spectra of ethylene chlorhydrin and *n*-propyl chloride in the vapour state at different temperatures above the boiling points, and in the liquid state at room temperature and at temperatures nearly equal to those of the vapour of corresponding liquids have been studied and compared with those reported for the solid state at low temperatures by previous workers. It is observed that the intensity-ratio of the two lines in 750 cm^{-1} and 662 cm^{-1} changes abruptly with the change from liquid to vapour phase in the case of ethylene chlorhydrin, and the same changes from about 1.0 to about 5.0 when the vapour at 130°C. is heated to 180°C. This intensity-ratio, however, changes only very slightly with change of temperature of the liquid from 30°C. to 130°C. In the case of *n*-propyl chloride the change in the intensity-ratio of the corresponding two lines is much smaller than that observed in the case of ethylene chlorhydrin, but the line 1452 cm^{-1} becomes much weaker and the frequency-shifts of the lines 728 cm^{-1} and 648 cm^{-1} increase to 742 cm^{-1} and 663 cm^{-1} respectively with vaporization of the liquid. It has been pointed out that the abrupt change in the intensity-ratio with vaporization of the liquid mentioned above cannot be explained on the assumption that two types of molecules co-exist in the liquid, the relative population of the molecules depending on their energy difference, and that a strong interaction between molecules in the liquid state is to be postulated to explain the above facts. It is also pointed out that the lines 742 cm^{-1} and 663 cm^{-1} observed in the case of *n*-propyl chloride in the vapour state are due to the single molecule and associated molecule respectively and the line 716 cm^{-1} observed in the case of the solid state is due to the associated molecules surrounded by regularly arranged neighbours.

INTRODUCTION

It was pointed out previously by the author (Mazumder, 1953) that the ratio of the intensity of the two lines 654 cm^{-1} and 755 cm^{-1} of ethylene dichloride in the vapour state at 135°C is 1 : 4.5 while this ratio has the value 1 : 5.0 at 170°C according to Morino *et al* (1942). These results indicated that the energy difference between the two forms of molecules in the vapour state was almost the same as that in the liquid state. This conclusion was contradictory to that arrived at earlier by Mizushima *et al* (1949). It was observed, however, that as the liquid at 130°C was transformed into vapour

* Communicated by Prof. S. C. Sirkar.

at 135°C the ratio of the intensities of the two lines changed from 1 : 2 to 1 : 4.5 and it was concluded that the ratio of the two forms of the molecule changes abruptly with vaporization of the liquid, and that a strong interaction between the neighbouring molecules taking place in the liquid state is responsible for this abrupt change. When the substance is solidified the line 654 cm^{-1} disappears and it was concluded by Mizushima *et al* (1938) that in the solid state the molecules are only of the 'trans' configuration. Similar phenomenon was also observed in the case of ethylene chlorhydrin and *n*-propyl chloride (Mizushima *et al*, 1940). They observed that the line 750 cm^{-1} of ethylene chlorhydrin disappears at low temperatures, and assuming that this line is given by the gauche form, they concluded that the molecules of ethylene chlorhydrin in the solid state are all of the 'trans' form, while in the case of *n*-propyl chloride in the solid state they are of the 'gauche' form, and that in the liquid state molecules of both trans and gauche forms are present. Recently, Mizushima *et al* (1951) investigated the Raman and infra red spectra of ethylene chlorhydrin in liquid and vapour states at different temperatures and attributing the line 750 cm^{-1} to the trans form they concluded that the molecules of the trans configuration increase in number with rise of temperature in the case of the vapour. So, according to this new assignment, the solid state of ethylene chlorhydrin would consist of molecules of gauche form only. The frequencies of vibration of different modes of the skeleton Cl-C-C-O have also been calculated for both the forms by these authors but although the calculated frequencies agree with observed frequencies in the case of gauche form, the agreement in the case of the trans form is poor. Mizushima *et al* (1951) measured the relative densities of the absorption bands 760 cm^{-1} and 669 cm^{-1} in the case of the vapour of ethylene chlorhydrin at different temperatures but similar data regarding the Raman spectrum of the substance were not available. On the other hand, the conclusion about disappearance of one of the two forms of the molecule with solidification was drawn by previous workers from the study of the Raman spectra. It was, therefore thought worthwhile to study the Raman spectra of ethylene chlorhydrin in the liquid and vapour states at high temperatures to find out whether in this case also any abrupt change takes place in the relative intensities of the two Raman lines 750 cm^{-1} and 662 cm^{-1} with vaporization of the liquid. As the Raman spectrum of *n*-propyl chloride also show some changes with solidification of the liquid, the Raman spectra of the compound in the liquid and vapour states at high temperatures have also been investigated for comparison.

EXPERIMENTAL

The experimental arrangement was similar to that used by the author in his previous investigation (Mazumder, 1953), excepting a little modification in the illuminating system. The liquids ethylene chlorhydrin and *n*-propyl chloride were distilled several times in vacuum before being introduced in the thickwalled Wood's

tube of special design (Mazumder, 1954). The temperature of the tube containing requisite quantity of the liquid was raised to about 180°C in the case of ethylene chlorhydrin (B. P. 128.8°C)and 100°C in the case of *n*-propyl chloride (B.P. 46.6°C), and the pressure developed inside the Wood's tube at those temperatures of the vapours of the corresponding liquids was about four atmospheres in each case. The liquid still left in the bulb at the tail after voporization was not more than 1 c.c. in volume. Two long glass tubes of diameter 6 cms. filled with distilled water were placed between the mercury arcs and the heater to focus the long mercury arcs on the axis of the Wood's tube. Two cylindrical reflectors of highly polished aluminium sheets were used to reflect back the light proceeding away from the Wood's tube, and this light also was focussed on to the axis of the Wood's tube. This improvement in the arrangement for illumination enhanced the intensity of the incident light so much that the time of exposure could be reduced to five days only.

The Adam Hilger two prism spectrograph used in the previous investigations was used in the present experiment also. Ilford Zenith plates were used to photograph the spectra. In both the cases the Raman spectra of the liquids at room temperature and at temperatures nearly equal to those of the vapours were also photographed for comparison. At least two spectrograms were obtained for the vapour phase of each of the two compounds in order to verify the changes observed in the first spectrogram in each case, and in the case of ethylene chlorhydrin spectrograms for the vapour at 130°C and 180°C were obtained.

RESULTS AND DISCUSSION

The Raman frequencies in wave number units are given in Tables I and II, in which the data for the solid state are also included for comparison. The spectrograms due to the substances in the vapour state at high temperatures and in the liquid state at tempeatures much above the boiling points are reproduced in Plate VIII.

It can be seen from Table I that in the case of ethylene chlorhydrin the ratio of the intensity of the two lines 662 cm^{-1} and 750 cm^{-1} changes abruptly as the liquid at 130°C is transformed into vapour at 130°C. This result is in complete disagreement with that reported by Mizushima *et al* (1951). They observed that the ratio of the densities of the absorption bands I_{760}/I_{669} increases from 0.55 to 0.68 as the temperature of ethylene chlorhydrin vapour is raised from 82°C to 155°C. In the case of Raman spectrum, however, the ratio I_{750}/I_{662} changes from 0.5 to about 0.6 when the temperature of the liquid is raised from 30°C to 130°C, but in the case of vapour at 130°C the ratio becomes almost equal to unity and at 180°C the ratio becomes about 5.0. It appears, therefore, that there is abrupt change in the ratio of the intensity of the two lines with vaporization of the liquid at 130°C, and a great change takes place again in the same intensity

TABLE I

Ethylene chlorhydrin, $Cl.CH_2.CH_2.OH$.

$\Delta\nu$ in kayser.

Liquid state		Mizushima *et al* (1940) Solid state	Vapour state	
at 30°C.	at 130°C.	at (Ca.–100°C.)	at 130°C.	at 180°C.
295 (1b) e	295 (½b) e	311 (0) e		
396 (2) e,k	396 (1) e,k			
476 (1) e,k	476 (½) e,k	471 (0) e		
662 (10) e,k	662 (5) e,k	659 (8) e,k,(i), f,g	662 (1) e,k	662 (0b) e,k
750 (5) e,k	750 (3) e,k		750 (1) e,k	750 (4) e,k
852 (3) e,k	852 (1) e,k	849 (3) e,k		825 (0) e
940 (2) e,k	940 (½) e,k	939 (3) e,k		
1034 (4) e,k	1034 (½b) e,k	1036 (3) e,k		
1078 (0) e,k		1083 (1) e,k		
		1130 (0) e,k		
		1171 (0) e,k		
1244 (4b) e,k		1246 (0) k		
		1387 (0) e,k		
1458 (6) e,k	1458 (2b) e,k	1451 (2) e,k		
2880 (2) e,k	2880 (1) e,k			
2928 (1) e,k		2934 (6) e,k,i		2928 (0) e,k
2958 (5b) e,k	2958 (3) e,k	2960 (8) e,k,i	2960 (3) e,k	2960 (6) e,k
3010 (3) e,k	3010 (1) e,k	3013 (5) e,k		

ratio when the temperature of the vapour is raised from 130°C to 180°C. If we assume that the two lines 662 cm^{-1} and 750 cm^{-1} are due to two configurations of the molecule then this great change in the ratio of the intensity of the two lines with change of temperature from 130°C to 180°C would indicate a large energy difference between the two forms of the molecule, but the small change in the intensity-ratio observed with the rise of temperature of the liquid, however, does not indicate such a large energy difference in the liquid state. So this postulate that the relative populations of the two types of molecules depend on the temperature is not supported by the observed facts. Also the abrupt change in the ratio of the intensity of the two lines with vaporization of the liquid at 130°C indicates

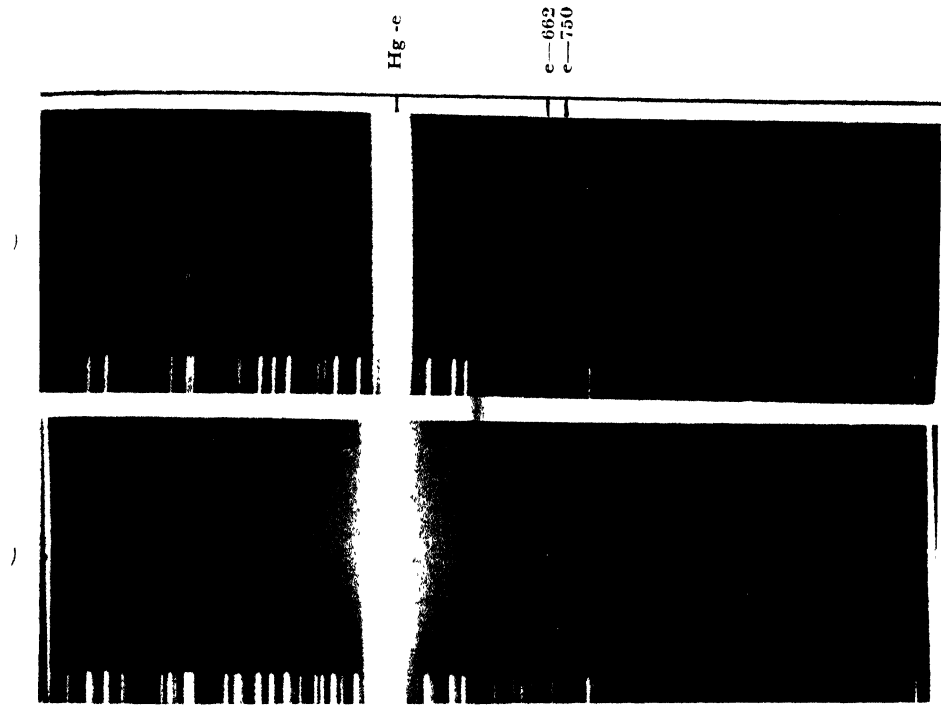

Fig. 1

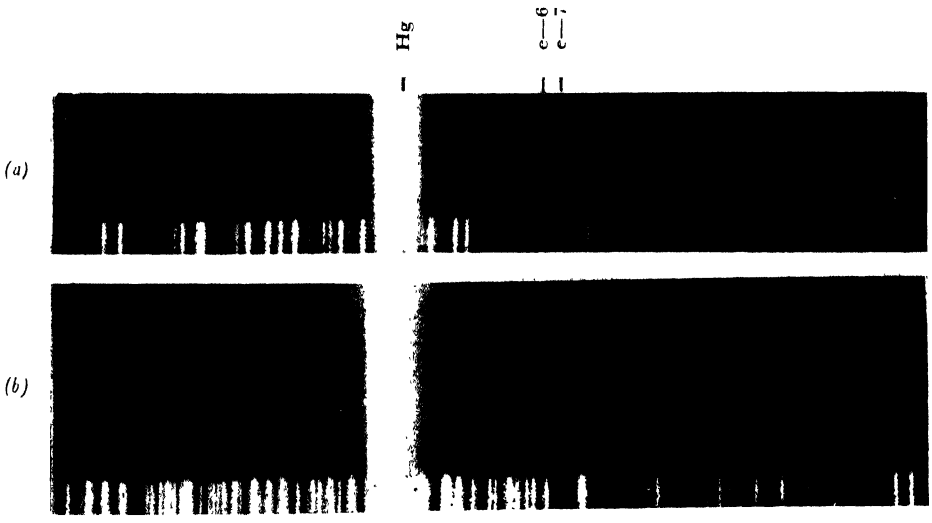

Fig. 2

Fig. 1. Ethylene chlorhydrin
(a) Liquid at 130°C
(b) Vapour at 180°C

Fig. 2. *n*-Propyl chloride
(a) Liquid at 100°C
(b) Vapour at 160°C

TABLE II

n-Propyl chloride, $CH_3CH_2CH_2Cl$.

$\Delta\nu$ in kayser

Liquid state		Mizushima *et al* (1940) Solid state	Vapour state
at 30°C.	at 100°C.	at (Ca.–150°C.)	at 100°C.
140 (0) e			146 (0b) e
		229 (0) e,(k)	
295 (1) e,k			
366 (7) e,k	366 (4) e,k	363 (5) e,(k)	368 (1) e,k
424 (1) e,k	424 (0) e,k		
648(10) ±e,k	648 (6) e,k	716 (7) e,k,i	663 (3) e,k
728 (5) e,k	728 (3) e,k		742 (2) e,k
791 (4) e,k	791 (2) e,k		
854 (2) e,k	854 (1) e,k		
894 (2) e,k	896 (1) e,k		
1026 (6) e,k	1026 (3) e,k	1029 (5) e,k	1030 (0b) e,k
1255 (3) e,k	1255 (1) e,k		
1452 (8b) e,k	1452 (4b) e,k	1441 (2) e,k	
2878 (6) e,k	2878 (4b) e,k	2870 (5) (e),k	2880 (2) e,k
		2894 (1) k	
2915 (3) e,k	2915 (2) e,k	2908 (1) (e),k	2915 (1) e,k
2937 (5) e,k	2937 (4) e,k	2941 (6) e,k	2959 (1) e,k
2960 (5) e,k	2960 (4) e,k	2975 (0) e,k	2970 (4) e,k
		2997 0) e,k	

that the intermolecular field in the liquid state is largely responsible for the creation of the two types of molecules in the liquid, and one of these two types may be a single molecule and the other an associated group of molecules. In the solid state the latter giving rise to the line 659 cm^{-1} is predominant. Thus these results clearly indicate that in the case of the molecules in the vapour state there is only one stable configuration and a second configuration is formed only in the state of

aggregation. In the liquid state both these configurations are present, while in the solid state the molecules are all in associated groups forming the second configuration.

In the case of *n*-propyl chloride, however, the situation seems to be more complicated. The change in the relative intensities of the lines 648 cm^{-1} and 728 cm^{-1} with change of temperature in the liquid is negligible and when the liquid at 100°C is vaporized at that temperature the ratio I_{728}/I_{648} increases very slightly. The line 1452 cm^{-1} which is more intense than the line 728 cm^{-1} in the case of the liquid at 100°C is absent in the case of the vapour at 100°C and the lines 2937 cm^{-1} and 2960 cm^{-1} shift respectively to 2959 cm^{-1} and 2970 cm^{-1}. This shows that the latter spectrum is due to the vapour only. On the other hand, as observed by Mizushima *et al* (1940), the line 649 cm^{-1} disappears when the liquid is solidified and cooled down to −150°C. Hence from these results they concluded earlier that in the solid state the *n*-propyl chloride molecules are all of gauche form and the ethylene chlorhydrin molecules are all of trans form and attributed the lines 649 cm^{-1} and 728 cm^{-1} of *n*-propyl chloride to trans and gauche configuration respectively and the corresponding lines 662 cm^{-1} and 750 cm^{-1} of ethylene chlorhydrin to the gauche and the trans configuration. They have, however, reversed their assignment recently (Mizushima *et al*, 1951) and have attributed the lines 750 cm^{-1} and 662 cm^{-1} of ethylene chlorhydrin to trans and gauche configuration respectively. So, according to this new assignment in the case of *n*-propyl chloride in the solid state all the molecules will be of trans configuration and both liquid and vapour states should consist of molecules of both the configurations. Evidently, the presence of the OH group in ethylene chlorhydrin molecule is responsible for this difference in behaviour of the two types of molecules. As both the lines 648 cm^{-1} and 728 cm^{-1} are polarised (Bishui, 1948) they are certainly due to the C-Cl vibration in two different types of molecules. If these two types are rotational isomers, the energy difference must be very small in the liquid and vapour states, as the relative intesities do not change very much with rise of temperature of the liquid. But the disappearance of one of these lines at 150°C cannot be due to the change of temperature alone, because the energy difference is very small. If on the other hand we assume that the associated molecules and the single molecule are the two types which produce these two lines, it is difficult to understand how the line 728 cm^{-1} increases in intensity both at low temperatures in the solid state and at high temperatures in the vapour state. Probably, the change in the value of the frequencies of the lines with change of state may provide some clue for the understanding of this phenomenon. The frequency of the Raman line 728 cm^{-1} observed at 30°C remains the same when the liquid is heated to 100°C, but it increases to 742 cm^{-1} when the liquid at 100°C is vaporized and apparently diminishes to 716 cm^{-1} when the liqud is solidified and cooled down to −150°C. No such shifts are observed in the case of ethylene chlorhydrin. So, it appears that since in the case of ethylene chlorhydrin the

C-Cl frequency is not affected appreciably by the intermolecular field the association between neighbouring molecules takes place through the OH group in the liquid state, while in the case of *n*-propyl chloride such association takes place through the Cl atom. If we now attribute the line 742 cm^{-1} to vibration in the single molecule and 663 cm^{-1} to that in the associated molecule in the vapour state, the influence of intermolecular field lowers these frequencies to 728 cm^{-1} and 648 cm^{-1} respectively in the liquid state. With solidification, however, further change takes place in the intermolecular field, as each C-Cl bond is surrounded by regularly arranged C-Cl groups in the lattice. The influence of these groups may be opposite to that of the formation of associated groups through the Cl atom. In that case we would except a frequency of C-Cl vibration intermediate between the frequencies of C-Cl vibration in the single molecule and the associated molecule respectively. This may be the reason why in the case of *n*-propyl chloride in the solid state the frequency of C-Cl vibration is observed to correspond to 716 cm^{-1} which is less than 742 cm^{-1} observed in the case of the single molecule and greater than 663 cm^{-1} given by the associated molecule in the case of vapour. It may be pointed out here that when association takes place through the Cl atom, the virtual bond may be much stronger than that formed through OH group. This may be the reason why in the case of *n*-propyl chloride associated molecules persist even in the vapour state, while in the case of ethylene chlorhydrin in the vapour state almost all the molecules are monomeric.

The C-Cl vibration frequencies observed in the case of *n*-propyl chloride in the vapour state agree closely with those observed in the case of ethylene chlorhydrin in the vapour state. This proves conclusively that the C-Cl stretching vibration in a single molecule has frequencies corresponding to 742 cm^{-1} and 750 cm^{-1} in the case of *n*-propyl chloride and ethylene chlorhydrin respectively. Any normal coordinate treatment should give this frequency as one of the normal modes of vibration. Since Misushima *et al* (1951) obtained 704 cm^{-1} as the calculated value for the 'trans' configuration of ethylene chlorhydrin molecule the potential constants used by them are not correct. Attempts have been made to find new potential constants for the obtained frequencies of the C-Cl vibration and the results will be published in a separate communication.

ACKNOWLEDGMENTS

The author is indebted to Professor S. C. Sirkar, D.Sc., F.N.I., for his kind interest and helpful guidance throughout the the progress of the work and to the Government of India for the award of a Senior research scholarship.

REFERENCES

Bishui, B. M., 1948, *Ind. J. Phys.*, **22**, 333.
Mazumder, M., 1953, *Ind. J. Phys.*, **27**, 405.

Mazumder, M., 1954, *Ind. J. Phys.*, **28**, 297.

Mizushima, S. and Morino, Y., 1938, *Proc. Ind. Acad. Sc.*, **8**, 315.

Mizushima, S., Morino, Y. and Nakamura, S., 1940, *Sc. Papers Inst. Phys. Chem. Research (Tokyo)*, **37**, 205.

Mizushima, S., Morino, Y., Watanabe, I., Simanouti, T. and Yamagauchi, S., 1949, *Jour. Chem. Phys.*, **17**, 592.

Mizushima, S., Shimanouchi, T., Miyazawa, T., Abe, K. and Yasumi, M., 1951, *Jour. Chem. Phys.*, **19**, 1477.

Morino, Y., Watanabe, I. and Mizushima, S., 1942, *Sc. Papers. Inst. Phys. Chem. Research (Tokyo)*, **29**, 396.